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(54) **Use of a specific catalyst for purifying exhaust gases from Diesel engines.**

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(73) Proprietor: NIPPON SHOKUBAI CO., LTD.
1-1, Koraibashi, 4-chome
Chuo-ku, Osaka-shi, Osaka-fu 541 (JP)

(72) Inventor: Horiuchi, Makoto
36-33, Aoyama
Himeji-shi, Hyogo-ken (JP)
Inventor: Inui, Satoshi
110-902, Yasuda 3-chome
Himeji-shi, Hyogo-ken (JP)
Inventor: Saito, Koichi
18-6, Yashiromiyamae-cho
Himeji-shi, Hyogo-ken (JP)

(74) Representative: Kraus, Walter, Dr. et al
Patentanwälte Kraus, Weisert & Partner
Thomas-Wimmer-Ring 15
D-80539 München (DE)

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Description

The present invention relates to the use of a specific catalyst for purifying exhaust gas from Diesel engines.

Recently, fine particulate substances (composed mainly of fine particles of solid carbon and of sulfur based substances such as sulfates, fine particles of liquid or solid high molecular weight hydrocarbons, etc., hereafter generically referred to as "fine particulate substances") in exhaust gases, particularly from Diesel engines, have attracted attention from a point view of keeping environmental hygiene. This is because the fine particulate substances are mostly no greater than 1 micrometers in particle diameter and float in the air readily, resulting in that they can be taken up into human bodies by aspiration. Therefore, it is naturally expected that legal control on the discharge of such fine particulate substances from Diesel engines will hereafter become severer.

On the other hand, it is true that the amount of the fine particulate substances discharged from Diesel engines have been reduced to some extent according as the pressure of fuel injection in Diesel engines increased and the control of timing of fuel injection was improved. However, components soluble in organic solvents (SOF) contained in the fine particulate substances and composed mainly of liquid high molecular weight hydrocarbons cannot be removed by the aforementioned improvement of the engine, resulting in the increase in the proportion of SOF in the fine particulate substances. Since SOF contains harmful components such as carcinogenic substances, it has become an important problem to remove SOF as well as the fine particulate substances.

As the method of removing the fine particulate substances, a method has been studied in which fine particulate substances in the exhaust gas from a Diesel engine are trapped with a catalyst having a catalytic substance for the combustion of carbon-based fine particles on a refractory three-dimensional structure such as ceramics foam, wire mesh, foamed metal, closed type ceramics honeycomb, open-flow-type ceramics honeycomb, or metal honeycomb, and the trapped fine particulate substances are heated by heating means such as exhaust gas produced under ordinary driving conditions or an electric heater to remove carbon-based fine particles by combustion.

Generally, it is desired that catalysts for purifying exhaust gas from Diesel engines have the following performances:

(a) They have high efficiencies of burning harmful components such as unburned hydrocarbons and carbon monoxide as well as carbon-based fine particles even at low temperatures;

(b) They have low capabilities of oxidizing sulfur dioxide (SO_2) generated by the sulfur component contained in gas oil used as a fuel into sulfur trioxide (SO_3) so that the production of sulfates (sulfur trioxide or sulfuric acid mists derived from sulfur dioxide) can be suppressed, and

(c) They can endure continuous operation under high loads (so-called high-temperature durability).

Hitherto, various proposals have been made with view to increasing the efficiency of burning and removing carbon-based fine particles.

For example, Japanese Patent Publication Laid-Open No. 24597/1980 discloses platinum family element-based catalysts such as rhodium (7.5%)/platinum alloy, platinum/palladium (50/50) mixture, palladium on tantalum oxide or cerium oxide, alloys of palladium and no more than 75% by weight of platinum, etc. Reportedly, these catalysts are also effective for removing SOF.

In addition thereto, Japanese Patent Publication Laid-Open Nos. 129030/1986, 149222/1986, and 146314/1986 disclose catalyst compositions containing palladium and rhodium as main active components to which are added alkali metals, alkaline earth metals, copper, lanthanum, zinc, manganese, etc. Japanese Patent Publication Laid-Open No. 82944/1984 discloses catalyst compositions composed of at least one metal selected from copper, alkali metals, molybdenum and vanadium, and at least one metal selected from platinum, rhodium and palladium, in combination.

As the catalyst for removing SOF in exhaust gas from Diesel engines, an open-type honeycomb noble metal-based oxide catalyst having throughholes parallel to the gas flow has been reported (cf. SAE Paper, 810263).

However, while all the aforementioned conventional catalysts are effective for the combustion and removal of carbon-based fine particles and the removal of SOF to some extent, they have defects that because of their high capability of oxidizing sulfur dioxide they increase the amount of sulfates produced to rather decrease the removal ratio of the entire fine particulate substances, and that new problems on environment arise because of the resulting sulfates.

As described above, no catalyst has been found yet that has the performances (a), (b) and (c) required for the catalysts for purifying exhaust gas from Diesel engines and the performance of removing SOF simultaneously.

Accordingly, an object of the present invention is to provide a catalyst for purifying exhaust gas from Diesel engines which can efficiently remove fine particulate substances in exhaust gas from Diesel engines. Said catalyst should have the capability of burning harmful components such as unburned hydrocarbons and carbon monoxide as well as carbon-based fine particles even at low temperatures, and which has a low capability of oxidizing sulfur dioxide to suppress the production of sulfates.

Said catalyst should be able to efficiently remove SOF in exhaust gas in Diesel engines and should have a good high-temperature durability and should be able to be mounted in Diesel cars without raising problems from practical viewpoint.

As a result of intensive investigations, the present inventors have found that a catalyst having a catalyst component-carrying layer made of a refractory three-dimensional structure having carried thereon a catalyst component containing (a) a refractory inorganic oxide, (b) palladium and/or platinum, and (c) rhodium in which the rhodium is contained selectively in an upper layer portion of the catalyst component-carrying layer is suitable for the above-described objects.

Therefore, the present invention provides the use of a catalyst made of a refractory three-dimensional structure having carried thereon a catalyst component-carrying layer containing (a) a refractory inorganic oxide, (b) at least one noble metal selected from palladium and platinum, and (c) rhodium, wherein said rhodium is contained only in an upper layer portion of said catalyst component-carrying layer corresponding to no more than 80% in thickness of said catalyst component-carrying layer, the amounts of the refractory inorganic oxide (a), the palladium and/or platinum (b), and the rhodium (c) being within the ranges of 3 to 300 g, larger than 0 and no larger than 6 g and 0.01 to 1 g, respectively, each per liter of the refractory three-dimensional structure, for purifying exhaust gas from Diesel engines.

As the refractory inorganic oxide (a), there can be used activated alumina, silica, titania, zirconia, silica-alumina, alumina-zirconia, alumina-titania, silica titania, silica-zirconia, titania-zirconia, zeolite, etc. Of these, there can be cited zirconia as the most suitable one that suppresses the production of sulfates and has a high selective oxidizability.

As the starting material for the platinum (b), there can be cited chloroplatinic acid, dinitrodiaminoplatinum, platinum tetramine chloride, platinum sulfide complex salts, etc. The starting material for the palladium (b) include palladium nitrate, palladium chloride, palladium tetramine chloride, palladium sulfide complex salts.

As the starting material for the rhodium (c), there can be cited rhodium nitrate, hexaamminerhodium chloride, rhodium sulfide complex salts, etc.

As the refractory three-dimensional structure, there can be used ceramics foams, open-flow-type ceramics honeycombs, wall-flow-type honeycomb monolith, open-flow-type metal honeycombs, foamed metals or metal meshes, etc. In particular, when exhaust gas from Diesel engines contains no more than 100 mg/m^3 of fine particulate substances and the content of SOF in the fine particulate substances is no less than 20 %, open-flow-type ceramics honeycombs or metal honeycombs are used advantageously as the refractory three-dimensional structure.

The catalyst of the present invention is characterized by having the aforementioned refractory three-dimensional structure which carries thereon the above-described catalyst components (a), (b) and (c), and contains rhodium only in an upper layer portion of the catalyst component-carrying layer, the upper layer portion corresponding to no more than 80% in thickness of the catalyst component-carrying layer. That is, in the catalyst of the present invention, rhodium is contained only in the upper layer portion of the catalyst component-carrying layer extending from the surface of the catalyst component-carrying layer in a direction of the thickness thereof, and corresponding to a region from above 0 % up to 80 %, in thickness of the catalyst component-carrying layer.

The method of making rhodium to be contained only in the upper layer portion of the catalyst component-carrying layer is not limited particularly, and the following method can be cited as an example.

That is, a catalyst component containing the refractory inorganic oxide (a) and the platinum and/or palladium (b) is applied to the refractory three-dimensional structure so as to be carried thereon to form a first layer, an then a catalyst component containing the refractory inorganic oxide (a) and the rhodium (c) is applied on the first layer to form a second layer to thereby form a catalyst component-carrying layer containing the rhodium (c) only in the second layer as the upper layer.

The second layer may further contain the platinum and/or palladium (b). However, the construction in which the first and second layers contain selectively the platinum and/or palladium (b) and the rhodium (c), respectively is more effective than the aforementioned construction as the form of using the noble metal.

The catalyst of the present invention may contain at least one element selected from rare earth elements such as lanthanum, cerium, praseodymium, neodymium and samarium in addition to the refractory inorganic oxide (a), the palladium and/or platinum (b), and the rhodium (c).

In the catalyst of the present invention, the amounts of the refractory inorganic oxide (a), the palladium and/or platinum (b), and the rhodium (c) which constitute the catalyst component-carrying layer are within the ranges of 3 to 300 g, larger than 0 and no larger than 6 g, preferably 0.01 to 6 g, and 0.01 to 1 g, respectively, each per liter of the refractory three-dimensional structure.

It is preferred that the amount of the aforementioned rare earth element added as required is within the range of 1 to 50 g per liter of the refractory three-dimensional structure.

As described above, in the catalyst of the present invention, the rhodium (c) must be contained as the essential component, and the upper layer portion containing the rhodium (c) occupies at most 80 % of total thickness of the catalyst component-carrying layer. When the catalyst contains no rhodium (c), or if the catalyst contains it, when the upper layer portion containing it occupies above 80 % of total thickness of the catalyst component-carrying layer, the catalyst has a low capability of removing fine particulate substances, thus failing to achieve the objects of the present invention.

There is no limitation on the method of preparing the catalyst of the present invention and specific examples thereof include the following methods.

(1) Powder of a refractory inorganic oxide is wet-ground to obtain slurry. A refractory three-dimensional structure is dipped in the slurry. After the removal of excessive slurry, the refractory three-dimensional is dried at 80 to 250 °C, and then calcined at 300 to 850 °C.

Next, the refractory three-dimensional structure is dipped in an aqueous solution containing a predetermined amount of a rhodium compound. After having absorbed and carried the rhodium compound thereon, excessive solution is removed from the refractory three-dimensional structure, which is dried at 80 to 250 °C and then calcined at 300 to 850 °C.

Finally, the refractory three-dimensional structure is dipped in an aqueous solution containing predetermined amounts of compounds of platinum and/or palladium, and after the removal of excessive solution, the refractory three-dimensional structure is dried at 80 to 250 °C and then calcined at 300 to 850 °C to obtain the objective catalyst.

(2) A refractory three-dimensional structure is dipped in a slurry containing compounds of platinum and/or palladium and a refractory inorganic oxide. After the removal of excessive slurry, the refractory three-dimensional structure is dried at 80 to 250 °C and calcined at 300 to 800 °C to form a first layer.

Then, the refractory three-dimensional structure having formed thereon the aforementioned first layer is dipped in a slurry containing a rhodium compound and a refractory inorganic oxide. After the removal of excessive slurry, the refractory three-dimensional structure is dried at 80 to 250 °C and then calcined at 300 to 850 °C to form a second layer to obtain the objective catalyst.

The catalyst of the present invention has a high capability of burning and removing harmful components such as unburned hydrocarbons and carbon monoxide as well as carbon-based fine particles even at low temperatures, and in addition has a low capability of oxidizing sulfur dioxide to suppress the production of sulfates. Therefore, the catalyst of the present invention is excellent in the reduction of the fine particulate substances in exhaust gas from Diesel engines, and the use of the catalyst of the present invention results in efficient purification of exhaust gas from Diesel engines.

The catalyst of the present invention is also excellent in the capability of removing SOF and is effective for purifying exhaust gas from Diesel engines.

Since it has a good high-temperature durability, the catalyst of the present invention can be mounted in Diesel cars without raising problems from practical viewpoint.

As described above the catalyst of the present invention is useful as a catalyst for purifying exhaust gas from Diesel Engines.

Hereafter, the present invention will be explained concretely by way of examples.

The distribution of rhodium in the catalyst component-carrying layer was measured using EPMA (Electron Probe Microanalyzer manufactured by Shimazu Seisakusho Co., Ltd.).

Example 1

Alumina (1 kg) having a specific surface area of 90 m^2/g was introduced in an aqueous solution of palladium nitrate containing 12.5g of palladium (hereafter, expressed as "12.5g of palladium nitrate (calculated as palladium)") dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 500 °C for 2 hours to obtain alumina palladium powder.

The powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped a cylindrical cordierite honeycomb carrier of 5.66 inch in diameter X 6.00 inch in length having about 300 cells/in^2 of cross-sectional area of open-flow-type gas communication cells. After the removal of excessive slurry, the carrier was dried at 150 °C for 2 hours and then calcined at 500 °C for 1 hour to obtain a structure having carried

thereon 81 g, per liter of the structure, of the alumina-palladium powder.

Next, alumina (1 kg) having a specific surface area of 90 m^2/g was introduced in an aqueous solution of 5 g of rhodium nitrate (calculated as rhodium) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 500 °C for 2 hours to obtain alumina-rhodium powder. The alumina-rhodium powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the aforementioned alumina-palladium-carrying structure. After the removal of excessive slurry, the carrier was dried at 150 °C for 3 hours and then calcined at 500 °C for 1 hour to obtain a catalyst having carried thereon 20.1 g, per liter of the structure, of the alumina-rhodium powder.

The resulting catalyst carried thereon alumina, palladium and rhodium in amounts of 100 g, 1 g and 0.1 g, respectively, per liter of the structure.

Rhodium was contained only in the upper layer portion corresponding to 30 % in thickness of the catalyst component-carrying layer.

Example 2

Alumina (1 kg) having a specific surface area of 150 m^2/g was introduced in an aqueous solution of 20 g of dinitrodiaminoplatinum (calculated as platinum) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 500 °C for 2 hours to obtain alumina-platinum powder.

The resulting powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the same cordierite honeycomb carrier as used in Example 1. After the removal of excessive slurry, the carrier was dried at 150 °C for 2 hours and then calcined at 500 °C for 1 hour to obtain a structure having carried thereon 51 g, per liter of the structure, of the alumina-platinum powder.

Next, alumina (1 kg) having a specific surface area of 90 m^2/g was introduced in an aqueous solution of 10 g of rhodium nitrate (calculated as rhodium) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 500 °C for 2 hours to obtain alumina-rhodium powder. The alumina-rhodium powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the afore-mentioned alumina-platinum-carrying structure. After the removal of excessive slurry, the carrier was dried at 150 °C for 3 hours and then calcined at 500 °C for 1 hour to obtain a catalyst having carried thereon 50.5 g, per liter of the structure, of the alumina-platinum powder.

The resulting catalyst carried thereon alumina, platinum and rhodium in amounts of 100 g, 1 g and 0.5 g, respectively, per liter of the structure.

Rhodium was contained only in the upper layer portion corresponding to 60% in thickness of the catalyst component-carrying layer.

Example 3

Alumina (1 kg) having a specific surface area of 150 m^2/g was introduced in an aqueous solution of 16.7 g of palladium nitrate (calculated as palladium) and 8.3 g of chloroplatinic acid (calculated as platinum) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 750 °C for 1 hour to obtain alumina-palladium-platinum powder.

The resulting powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the same cordierite honeycomb carrier as used in Example 1. After the removal of excessive slurry, the carrier was dried at 150 °C for 2 hours and then calcined at 500 °C for 1 hour to obtain a structure having carried thereon 62 g, per liter of the structure, of the alumina-palladium-platinum powder.

Next, alumina (1 kg) having a specific surface area of 120 m^2/g was introduced in an aqueous solution of 12.5 g of hexaamminerhodium chloride (calculated as rhodium) dissolved in deionized water. After being stirred well, the mixture was dried at 180 °C for 3 hours, and then calcined at 500 °C for 1 hour to obtain alumina-rhodium powder. The alumina-rhodium powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the aforementioned alumina-palladium-platinum-carrying structure. After the removal of excessive slurry, the carrier was dried at 150 °C for 2 hours and then calcined at 500 °C for 1 hour to obtain a catalyst having carried thereon 40.5 g, per liter of the structure, of the alumina-rhodium powder.

The resulting catalyst carried thereon alumina, palladium, platinum and rhodium in amounts of 100 g, 1 g, 0.5 g and 0.5 g, respectively, per liter of the structure.

Rhodium was contained only in the upper layer portion corresponding to 50 % in thickness of the catalyst component-carrying layer.

Example 4

Zirconia (1 kg) having a specific surface area of 80 m^2/g was introduced in an aqueous solution of 20 g of palladium nitrate (calculated as palladium) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 6 hours, and then calcined at 700 °C for 1 hour to obtain zirconia-palladium powder.

The resulting powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the same cordierite honeycomb carrier as used in Example 1. After the removal of excessive slurry, the carrier was dried at 150 °C for 3 hours and then calcined at 500 °C for 1 hour to obtain a structure having carried thereon 51 g, per liter of the structure, of the zirconia-palladium powder.

Next, zirconia (1 kg) having a specific surface area of 80 m^2/g was introduced in an aqueous solution of 20 g of rhodium nitrate (calculated as rhodium) dissolved in deinonized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 500 °C for 1 hour to obtain zirconia-rhodium powder.

The zirconia-rhodium powder was wet-ground to form a slurry. In the slurry was dipped the aforementioned zirconia-rhodium-carrying structure. After the removal of excessive slurry, the carrier was dried at 180 °C for 2 hours and then calcined at 700 °C for 2 hours to obtain a catalyst having carried thereon 5.1 g, per liter of the structure, of the zirconia-rhodium powder.

The resulting catalyst carried thereon zirconia, palladium and rhodium in amounts of 55 g, 1 g and 0.1 g, respectively, per liter of the structure.

Rhodium was contained only in the upper layer portion corresponding to 20 % in thickness of the catalyst component-carrying layer.

Example 5

Zirconia (1 kg) having a specific surface area of 60 m^2/g was introduced in an aqueous solution of 25 g of palladium chloride (calculated as palladium) and 165 g of praseodymium nitrate dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 6 hours, and then calcined at 500 °C for 2 hours to obtain zirconia-palladium-praseodymium oxide powder.

The resulting powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped a cylindrical stainless steel honeycomb carrier of 5.66 inch in diameter X 6.0 inch in length having about 300 cells/in^2 of cross-sectional area of open-flow-type gas communication cells. After the removal of excessive slurry, the carrier was dried at 180 °C for 2 hours and then calcined at 650 °C for 3 hours to obtain a structure having carried thereon 87 g, per liter of the structure, of the zirconia-palladium-praseodymium oxide powder.

Next, zirconia (1 kg) having a specific surface area of 90 m^2/g was introduced in an aqueous solution of 5 g of rhodium nitrate (calculated as rhodium) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 500 °C for 2 hours to obtain zirconia-rhodium powder.

The resulting powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the aforementioned zirconia-palladium-praseodymium oxide-carrying structure. After the removal of excessive slurry, the carrier was dried at 150 °C for 6 hours and then calcined at 400 °C for 1 hour to obtain a catalyst having carried thereon 20.1 g, per liter of the structure, of the zirconia-rhodium powder.

The resulting catalyst carried thereon zirconia, palladium, rhodium and praseodymium oxide in amounts of 100 g, 2 g, 0.1 g and 5 g, respectively, per liter of the structure.

Rhodium was contained only in the upper layer portion corresponding to 30% in thickness of the catalyst component-carrying layer.

Example 6

Alumina (1 kg) having a specific surface area of 150 m^2/g was introduced in an aqueous solution of 20 g of dinitrodiaminoplatinum (calculated as platinum) and 1,510 g of cerium nitrate dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 6 hours, and then calcined at 500 °C for 2 hours to obtain alumina-platinum-ceria powder.

The powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped a cylindrical cordierite honeycomb carrier of 5.66 inch in diameter X 6.00 inch in length having about 200 cells/in^2 of cross-sectional area of open-flow-type gas communication cells. After the removal of excessive slurry, the carrier as dried at 150 °C for 3 hours and then calcined at 400 °C for 2 hours to obtain a structure having carried thereon 81 g, per liter of the structure, of the alumina-platinum-ceria powder.

Next, alumina (1 kg) having a specific surface area of 150 m^2/g was introduced in an aqueous solution of 5 g of rhodium nitrate (calculated as rhodium) and 266 g of lanthanum nitrate dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 500 °C for 1 hour to obtain alumina-rhodium-lanthanum oxide powder.

The alumina-rhodium powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the aforementioned alumina-platinum-ceria-carrying structure. After the removal of excessive slurry, the carrier was dried at 150 °C for 3 hours and then calcined at 600 °C for 1 hour to obtain a catalyst having carried thereon 110.5 g, per liter of the structure, of the alumina-rhodium-lanthanum oxide powder.

The resulting catalyst carried thereon alumina, platinum, rhodium, ceria and lanthanum oxide in amounts of 150 g, 1 g, 0.5 g, 30 g and 10 g, respectively, per liter of the structure.

Rhodium was contained only in the upper layer portion corresponding to 70 % in thickness of the catalyst component-carrying layer.

Example 7

Silica (1 kg) having a specific surface area of 55 m^2/g was introduced in an aqueous solution of 20 g of palladium nitrate (calculated as palladium) and 6 g of chloroplatinic acid (calculated as platinum) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 600 °C for 2 hours to obtain silica-palladium-platinum powder.

The resulting powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the same cordierite honeycomb carrier as used in Example 5. After the removal of excessive slurry, the carrier was dried at 150 °C for 3 hours and then calcined at 500 °C for 1 hour to obtain a structure having carried thereon 51.3 g, per liter of the structure, of the silica-palladium-platinum powder.

Next, titania (1 kg) having a specific surface area of 65 m^2/g was introduced in an aqueous solution of 50 g of rhodium nitrate (calculated as rhodium) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 400 °C for 1 hour to obtain titania-rhodium powder.

The resulting powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the aforementioned silica-palladium-platinum-carrying structure. After the removal of excessive slurry, the carrier was dried at 150 °C for 3 hours and then calcined at 500 °C for 1 hour to obtain a catalyst having carried thereon 10.5 g, per liter of the structure, of the titania-rhodium powder.

The resulting catalyst carried thereon silica, titania, palladium, platinum and rhodium in amounts of 50 g, 10 g, 1 g, 0.3 g and 0.5 g, respectively, per liter of the structure.

Rhodium was contained only in the upper layer portion corresponding to 25 % in thickness of the catalyst component-carrying layer.

Example 8

Alumina (1 kg) having a specific surface area of 150 m^2/g was introduced in an aqueous solution of 25 g of palladium sulfide complex salt (calculated as palladium) and 12.5 g of platinum sulfide complex salt (calculated as platinum) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 800 °C for 5 hours to obtain alumina-palladium-platinum powder.

The resulting powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the same cordierite honeycomb carrier as used in Example 1. After the removal of excessive slurry, the carrier was dried at 150 °C for 6 hours and then calcined at 500 °C for 1 hour to obtain a structure having carried thereon 41.5 g, per liter of the structure, of the alumina-palladium-platinum powder.

Next, zirconia (1 kg) having a specific surface area of 40 m^2/g was introduced in an aqueous solution of 8.3 g dinitrodiaminoplatinum (calculated as platinum) and 8.3 g of rhodium nitrate (calculated as rhodium) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 6 hours, and then calcined at 750 °C for 4 hours to obtain zirconia-platinum-rhodium powder.

The resulting powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the aforementioned alumina-palladium-platinum-carrying structure. After the removal of excessive slurry, the carrier was dried at 150 °C for 3 hours and then calcined at 400 °C for 2 hours to obtain a catalyst having carried thereon 61.0 g, per liter of the structure, of the zirconia-palladium-platinum powder.

The resulting catalyst carried thereon alumina, zirconia, palladium, platinum and rhodium in amounts of 40 g, 60 g, 1 g, 1 g and 0.5 g, respectively, per liter of the structure.

Rhodium was contained only in the upper layer portion corresponding to 70 % in thickness of the catalyst component-carrying layer.

Example 9

One kg of alumina having a specific surface area of 150 m^2/g was weighed and wet-ground with water to form a slurry. In the slurry was dipped a cylindrical cordierite honeycomb carrier of 5.66 inch in diameter X 6.00 inch in length having about 400 cells/in^2 of cross-sectional area of open-flow-type gas communication cells. After the removal of excessive slurry, the carrier was dried at 150 °C for 3 hours and then calcined at 500 °C for 1 hour to obtain a structure having carried thereon the alumina powder.

The structure was dipped in 2.5 liters of an aqueous rhodium nitrate solution containing 0.4 g of rhodium at 80 °C to adsorb rhodium thereon. After the removal of excessive solution, the structure was dried at 150 °C for 3 hours, and then calcined at 700 °C for 1 hour to have rhodium carried on the aforementioned alumina-carrying structure.

Next, the above-described alumina-rhodium-carrying structure was dipped in 2.5 liters of an aqueous solution of 3.8 g of chloroplatinic acid (calculated as platinum) and 38.5 g of palladium chloride (calculated as palladium) dissolved in deionized water. After the removal of excessive solution, the structure was dried at 150 °C for 3 hours, and then calcined at 500 °C for 2 hours to obtain a catalyst.

The resulting catalyst carried thereon alumina, palladium, platinum and rhodium in amounts of 55 g, 2 g, 0.2 g and 0.2 g, respectively, per liter of the structure.

Rhodium was contained only in the upper layer portion corresponding to 20 % in thickness of the catalyst component-carrying layer.

Example 10

A catalyst was obtained in the same manner as in Example 4 except that instead of the cordierite honeycomb carrier, a cylindrical cordierite ceramics foam of 5.66 inch in diameter X 6.00 inch in length having about 12 cells/in of cells formed of ceramics skeleton and having a void ratio of about 90 % was used.

The resulting catalyst carried thereon zirconia, palladium and rhodium in amounts of 55 g, 1 g and 0.1 g, respectively, per liter of the structure.

Rhodium was contained only in the upper layer portion corresponding to 20 % in thickness of the catalyst component-carrying layer.

Comparative Example 1

Alumina (1 kg) having a specific surface area of 150 m^2/g was introduced in an aqueous solution of 10 g of palladium nitrate (calculated as palladium) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 500 °C for 1 hour to obtain alumina-palladium powder.

The resulting powder (1 kg) was wet-ground to form a slurry. In the slurry was dipped the same cordierite honeycomb carrier as used in Example 1. After the removal of excessive slurry, the carrier was dried at 150 °C for 3 hours and then calcined at 500 °C for 1 hour to obtain a catalyst.

The resulting catalyst carried thereon alumina and palladium in amounts of 100 g and 1 g, respectively, per liter of the structure.

Comparative Example 2

A catalyst was obtained in the same manner as in Comparative Example 1 except that dinitroaminoplatinum was used instead of palladium nitrate.

The resulting catalyst carried thereon alumina and platinum in amounts of 100 g and 1 g, respectively, per liter of the structure.

Comparative Example 3

Alumina (1 kg) having a specific surface area of 150 m^2/g was introduced in an aqueous solution of 10 g of palladium nitrate (calculated as palladium) and 10 g of chloroplatinic acid (calculated as platinum) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 750 °C for 1 hour to obtain alumina-palladium-platinum powder.

Subsequently, a catalyst was obtained in the same manner as in Comparative Example 1.

The resulting catalyst carried thereon alumina, palladium and platinum in amounts of 100 g, 1 g and 1 g, respectively, per liter of the structure.

Comparative Example 4

Alumina (1 kg) having a specific surface area of 90 m^2/g was introduced in an aqueous solution of 10 g of palladium nitrate (calculated as palladium) and 0.1 g of rhodium nitrate (calculated as rhodium) dissolved deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 500 °C for 2 hours to obtain alumina-palladium-rhodium powder.

Subsequently, a catalyst was obtained in the same manner as in Comparative Example 1.

The resulting catalyst carried thereon alumina, palladium and rhodium in amounts of 100 g, 1 g and 0.1 g, respectively, per liter of the structure.

Comparative Example 5

Alumina (1 kg) having a specific surface area of 150 m^2/g was introduced in an aqueous solution of 10 g of dinitrodiaminoplatinum (calculated as platinum) and 5 g of rhodium nitrate (calculated as rhodium) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 500 °C for 1 hour to obtain alumina-platinum-rhodium powder.

Subsequently, a catalyst was obtained in the same manner as in Comparative Example 1.

The resulting catalyst carried thereon alumina, platinum and rhodium in amounts of 100 g, 1 g and 0.5 g, respectively, per liter of the structure.

Comparative Example 6

Alumina (1 kg) having a specific surface area of 150 m^2/g was introduced in an aqueous solution of 10 g of palladium nitrate (calculated as palladium), 5 g of chloroplatinic acid (calculated as platinum) and 5 g of hexaamminerhodium chloride (calculated as rhodium) dissolved in deionized water. After being stirred well, the mixture was dried at 150 °C for 3 hours, and then calcined at 750 °C for 1 hour to obtain alumina-palladium-platinum-rhodium powder.

Subsequently, a catalyst was obtained in the same manner as in Comparative Example 1.

The resulting catalyst carried thereon alumina, palladium, platinum and rhodium in amounts of 100 g, 1 g, 0.5 g and 0.5 g, respectively, per liter of the structure.

Table 1 shows the amounts of the respective components and the proportions of the thickness of the upper layer portion in which rhodium was contained to the thickness of the catalyst component-carrying layer for the respective catalysts obtained in Examples 1 to 11 and Comparative Examples 1 to 6.

Table 1 *) Proportion of the thickness of the upper layer portion containing rhodium to the thickness of the catalyst component-carrying layer

Run No.	Refractory Inorganic Oxide (a)		Noble Metal (b)		Rhodium (c)	Additional Element		Refractory Three-Dimensional Structure	Proportion of Thickness*) (%)
	Kind	Amount (g/l of carrier)	Kind	Amount (g/l of carrier)	Amount (g/l of carrier)	Kind	Amount (g/l of carrier)		
Ex. 1	Al_2O_3	100	Pd	1	0.1	-	-	Ceramics honeycomb	30
Ex. 2	Al_2O_3	100	Pt	1	0.5	-	-	Ceramics honeycomb	60
Ex. 3	Al_2O_3	100	Pd/Pt	1/0.5	0.5	-	-	Ceramics honeycomb	50
Ex. 4	ZrO_2	55	Pd	1	0.1	-	-	Ceramics honeycomb	20
Ex. 5	ZrO_2	100	Pd	2	0.1	Pr_6O_{11}	5	Metal honeycomb	30
Ex. 6	Al_2O_3	150	Pt	1	0.5	CeO_2/ La_2O_3	30/10	Ceramics honeycomb	70
Ex. 7	SiO_2/ TiO_2	50/10	Pd/Pt	1/0.3	0.5	-	-	Metal honeycomb	25
Ex. 8	Al_2O_3/ ZrO_2	40/60	Pd/Pt	1/1	0.5	-	-	Ceramics honeycomb	70

- continued -

Table 1 (continued)

Run No.	Refractory Inorganic Oxide (a)		Noble Metal (b)		Rhodium (c)	Additional Element		Refractory Three-Dimensional Structure	Proportion of Thickness*) (%)
	Kind	Amount (g/l of carrier)	Kind	Amount (g/l of carrier)	Amount (g/l of carrier)	Kind	Amount (g/l of carrier)		
Ex. 9	Al_2O_3	55	Pd/Pt	2/0.2	0.2	-	-	Ceramics honeycomb	20
Ex. 10	ZrO_2	55	Pd	1/0.1	0.1	-	-	Ceramics foam	20
Comp. Ex. 1	Al_2O_3	100	Pd	1	-	-	-	Ceramics honeycomb	-
Comp. Ex. 2	Al_2O_3	100	Pt	1	-	-	-	Ceramics honeycomb	-
Comp. Ex. 3	Al_2O_3	100	Pd/Pt	1/1	-	-	-	Ceramics honeycomb	-
Comp. Ex. 4	Al_2O_3	100	Pd	1	0.1	-	-	Ceramics honeycomb	100
Comp. Ex. 5	Al_2O_3	100	Pt	1	0.5	-	-	Ceramic honeycomb	100
Comp. Ex. 6	Al_2O_3	100	Pd/Pt	1/0.5	0.5	-	-	Ceramics honeycomb	100

*) Proportion of the thickness of the upper layer portion containing rhodium to the thickness of the catalyst component-carrying layer

Reference Example

Evaluation was made on the performance of purifying exhaust gas from Diesel engines for the respective catalysts obtained in Examples 1 to 10 and Comparative Examples 1 to 6.

Using a supercharged direct injection-type Diesel engine (4 valves, 2,800 cc) and gas oil with a sulfur content of 0.47 % by weight as a fuel, the following experiments were carried out.

Each catalyst was attached to an exhaust pipe from the aforementioned engine, and durability tests were practiced for 300 hours under the conditions of full load at an engine rotation number of 2,500 rpm and catalyst inlet temperature of 600 ° C.

Thereafter, the contents of fine particulate substances in the exhaust gas before entrance in the catalyst bed (inlet) and after getting out of the catalyst bed (outlet) were measured using a conventional dilution tunnel method under the conditions an engine rotation number of 2,000 rpm, a torque of 8.5 kg•m, and a catalyst inlet temperature of 300 ° C to obtain a degree of removal of fine particulate substances, i.e., purification ratio (%). At the same time, analysis was made on sulfur dioxide, gaseous hydrocarbons, an carbon monoxide in the exhaust gas before entering the catalyst bed and after passage through the catalyst bed to obtain their conversions.

Table 2 show the results obtained.

Table 2

Run No.	Content of Fine Particulate Substance in Exhaust Gas: Inlet (mg/m^3)	Content of Fine Particulate Substance in Exhaust Gas: Outlet (mg/m^3)	Purification Ratio of Fine Particulate Substance (%)	Conversion of Hydrocarbon (%)	Conversion of Carbon Monoxide (%)	Conversion of Sulfur Dioxide (%)
Ex. 1	40.5	20.1	50	83	68	0.1
Ex. 2	39.8	22.3	44	84	79	0.4
Ex. 3	40.2	19.2	52	85	82	0.2
Ex. 4	38.5	16.4	57	85	76	0.0
Ex. 5	41.3	14.9	64	87	73	0.0
Ex. 6	37.9	20.9	45	82	83	0.2
Ex. 7	40.0	20.7	48	78	74	0.1
Ex. 8	38.7	26.2	32	84	85	0.5
Ex. 9	38.9	21.6	44	81	78	0.3
Ex. 10	40.2	19.0	53	81	69	0.0

- continued -

Table 2 (Continued)

Run No.	Content of Fine Particulate Substance in Exhaust Gas		Purification Ratio of Fine Particulate Substance (%)	Conversion of Hydrocarbon (%)	Conversion of Carbon Monoxide (%)	Conversion of Sulfur Dioxide (%)
	Inlet (mg/m^3)	Outlet (mg/m^3)				
Comp. Ex. 1	41.0	54.2	-3.2	81	69	3.7
Comp. Ex. 2	39.5	591	-1,396	83	81	58
Comp. Ex. 3	37.8	327	-765	86	83	32
Comp. Ex. 4	42.1	41.9	0.5	72	37	2.3
Comp. Ex. 5	40.6	457	-1,025	69	62	44
Comp. Ex. 6	38.7	234	-505	76	64	21

Claims

1. Use of a catalyst for purifying exhaust gas from Diesel engines made of a refractory three-dimensional structure having carried thereon a catalyst component-carrying layer containing (a) a refractory inorganic oxide, (b) at least one noble metal selected from palladium and platinum, and (c) rhodium, wherein said rhodium is contained only in an upper layer portion of said catalyst component-carrying layer corresponding to no more than 80% in thickness of said catalyst component-carrying layer, the

amounts of the refractory inorganic oxide (a), the palladium and/or platinum (b), and the rhodium (c) being within the ranges of 3 to 300 g, larger than 0 and no larger than 6 g and 0.01 to 1 g, respectively, each per liter of the refractory three-dimensional structure.

2. Use as claimed in claim 1, wherein said catalyst component-carrying layer comprises a first layer contacting said refractory three-dimensional structure and a second layer provided on said first layer, said first layer comprising a first catalyst component composed of said refractory inorganic oxide (a), and said at least one noble metal selected from palladium and platinum (b), and said second layer comprising a second catalyst component composed of said rhodium (c), and optionally said refractory inorganic oxide (a) and/or said at least one noble metal (b).

3. Use as claimed in Claim 1 or 2, wherein said refractory inorganic oxide is at least one member selected from the group consisting of alumina, silica, titania, zirconia, silica-alumina, alumina-zirconia, alumina-titania, silica-titania, silica-zirconia, titania-zirconia and zeolite.

4. Use as claimed in Claim 1 or 2, wherein said refractory inorganic oxide is zirconia.

5. Use as claimed in anyone of claims 1 to 4, wherein said refractory three-dimensional structure is a ceramics foam, an open-flow-type ceramics honeycomb, a wall-flow-type honeycomb monolith, an open-flow-type metal honeycomb, a metal foam or a metal mesh.

6. Use as claimed in anyone of claims 1 to 4, wherein said refractory three-dimensional structure is an open-flow-type ceramics honeycomb or an open-flow-type metal honeycomb.

Patentansprüche

1. Verwendung eines Katalysators für die Reinigung der Abgase von Dieselmotoren, wobei dieser aus einer hitzebeständigen dreidimensionalen Struktur besteht, die auf ihrer Oberfläche eine Katalysatorkomponenten-tragende Schicht trägt, die (a) ein hitzebeständiges anorganisches Oxid, (b) mindestens ein Edelmetall, ausgewählt aus Palladium und Platin, und (c) Rhodium enthält, wobei das Rhodium nur im oberen Schichtanteil der Katalysatorkomponenten-tragenden Schicht, der nicht mehr als 80% der Dicke der Katalysatorkomponenten-tragenden Schicht entspricht, enthalten ist, und die Mengen des hitzebeständigen anorganischen Oxids (a), des Palladiums und/oder Platins (b), und des Rhodiums (c), jeweils pro Liter der hitzebeständigen dreidimensionalen Struktur in den Bereichen 3 bis 300 g bzw. größer als 0 und nicht größer als 6 g, beziehungsweise 0,01 bis 1 g, liegen.

2. Verwendung nach Anspruch 1, dadurch **gekennzeichnet**, daß die Katalysatorkomponenten-tragende Schicht eine erste Schicht, die die hitzebeständige dreidimensionale Struktur kontaktiert und eine zweite auf der ersten Schicht befindliche Schicht umfaßt, wobei die genannte erste Schicht eine erste Katalysatorkomponente, bestehend aus dem hitzebeständigen anorganischen Oxid (a) und mindestens einem Edelmetall, ausgewählt aus Palladium und Platin (b), umfaßt, und die zweite Schicht eine zweite Katalysatorkomponente, bestehend aus dem Rhodium (c) und gegebenenfalls dem hitzebeständigen anorganischen Oxid (a) und/oder dem mindestens einem Edelmetall (b), umfaßt.

3. Verwendung nach Anspruch 1 oder 2, dadurch **gekennzeichnet**, daß das hitzebeständige anorganische Oxid mindestens ein Bestandteil, ausgewählt aus der Gruppe bestehend aus Aluminiumoxid, Siliciumdioxid, Titandioxid, Zircondioxid, Siliciumdioxid-Aluminiumoxid, Aluminiumoxid-Zircondioxid, Aluminiumoxid-Titandioxid, Siliciumdioxid-Titandioxid, Siliciumdioxid-Zircondioxid, Titandioxid-Zircondioxid und Zeolith ist.

4. Verwendung nach Anspruch 1 oder 2, dadurch **gekennzeichnet**, daß das hitzebeständige anorganische Oxid Zircondioxid ist.

5. Verwendung nach einem der Ansprüche 1 bis 4, dadurch **gekennzeichnet**, daß die hitzebeständige dreidimensionale Struktur ein Keramikschaum, eine Keramikwabenstruktur vom Open-Flow-Typ, ein Monolith mit Wabenstruktur vom Wall-Flow-Typ, eine Metallwabenstruktur vom Open-Flow-Typ, ein Metallschaum oder ein Metallsieb ist.

6. Verwendung nach einem der Ansprüche 1 bis 4, dadurch **gekennzeichnet**, daß die hitzebeständige dreidimensionale Struktur eine Keramikwabenstruktur vom Open-Flow-Typ oder eine Metallwabenstruktur vom Open-Flow-Typ ist.

Revendications

1. Utilisation dans un catalyseur pour purifier et épurer du gaz s'échappant de moteurs Diesel, catalyseur constitué d'une structure tridimensionnelle réfractaire portant une couche porteuse d'un ou plusieurs constituants de catalyseur et contenant (a) un oxyde minéral réfractaire (b) au moins un métal noble choisi parmi le palladium et le platine, et (c) du rhodium, ledit rhodium étant contenu seulement dans une partie de couche supérieure de ladite couche portant un ou des constituant(s) de catalyseur, cette partie correspondant à une proportion non supérieure à 80 % de l'épaisseur de ladite couche porteuse du ou des constituants de catalyseur, les quantités de l'oxyde minéral réfractaire (a), du palladium et/ou du platine (b) et du rhodium (c) se situant entre 3 et 300 g, plus de 0 et pas plus de 6 g, et 0,01 à 1 g, respectivement, chaque teneur étant par litre de la structure tridimensionnelle réfractaire.

2. Utilisation selon la revendication 1, dans laquelle ladite couche portant le ou les constituants de catalyseur comprend une première couche au contact de ladite structure tridimensionnelle réfractaire et une seconde couche placée sur ladite première couche, ladite première couche comprenant un premier constituant de catalyseur composé dudit oxyde minéral réfractaire (a) et dudit ou desdits au moins un métal noble choisi parmi le palladium et le platine (b), et ladite seconde couche comprenant un second constituant de catalyseur composé dudit rhodium (c) et éventuellement dudit oxyde minéral réfractaire (a) et/ou dudit au moins un métal noble (b).

3. Utilisation selon la revendication 1 ou 2, dans laquelle ledit oxyde minéral réfractaire est au moins un membre choisi dans l'ensemble consistant en l'alumine, la silice, l'oxyde de titane, l'oxyde de zirconium, de la silice-alumine, de l'alumine/oxyde de zirconium, de l'alumine/oxyde de titane, de la silice/oxyde de titane, de la silice/oxyde de zirconium, de l'oxyde de titane/oxyde de zirconium et une zéolite.

4. Utilisation selon la revendication 1 ou 2, dans le cas de laquelle ledit oxyde minéral réfractaire est de l'oxyde de zirconium.

5. Utilisation selon l'une quelconque des revendications 1 à 4, dans le cas de laquelle ladite structure tridimensionnelle réfractaire est une mousse de matière céramique, un nid d'abeilles en matière céramique du type à écoulement libre ou ouvert, un monolithe en nid d'abeilles de type à écoulement le long d'une paroi, un nid d'abeilles en métal de type à écoulement libre ou ouvert, une mousse de métal, ou une toile métallique.

6. Utilisation selon l'une quelconque des revendications 1 à 4, dans le cas de laquelle ladite structure tridimensionnelle réfractaire est un nid d'abeilles en matière céramique de type à écoulement libre ou ouvert ou un nid d'abeilles en métal du type à écoulement libre ou ouvert.